Supporting materials

Lanthanide complexes for second order nonlinear optics: evidence for the direct contribution of f electrons to the quadratic hyperpolarizability.

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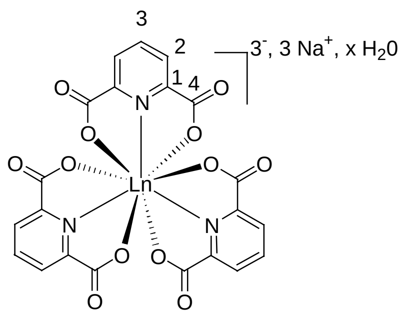

Table S1. Elemental analysis [Ln(dipic)$_3$][Na]$_3$,x(H$_2$0)

Ln (*x*)	Wt% C[a] exp (th)	Wt% H[a] exp (th)	Wt% N[a] exp (th)	C/Ln[b] (th:21)	Na/Ln[b] (th:3)
Y (*x* = 6)	33.32 (33.13)	2.76 (2.78)	5.57 (5.52)	20.7	3.1
La (*x* = 3)	32.59 (33.31)	1.99 (2.00)	5.58 (5.55)	21.8	3.2
Nd (*x* = 4)	32.29 (32.31)	2.09 (2.20)	5.38 (5.38)	20.3	3.1
Eu (*x* = 4)	31.60 (32.00)	2.33 (2.17)	5.35 (5.33)	20.4	2.7
Dy (*x* = 5)	30.82 (30.88)	2.59 (2.34)	5.06 (5.14)	20.0	3.8
Er (*x* = 5)	31.07 (30.70)	2.41 (2.33)	5.18 (5.11)	19.9	3.6
Lu (*x* = 5)	30.51 (30.31)	2.65 (2.31)	5.20 (5.07)	19.0	3.2

a: determined by elemental analysis; b: determined by microfluorescence X.

Table S2. ^{13}C RMN data expressed in ppm (D_2O, 200.13 MHz, RT) for $[Ln(dipic)_3][Na]_3$,x(H_20), in *italic* data obtained from Piguet et al. *Inorg.Chem.* **2002**, *41*, 1436-1445.

Ln	C1	C2	C3	C4
Y	148.5 (*151.70*)	125.6 (*128.81*)	140.6 (*143.92*)	171.7 (*173.08*)
La	149.9 *(150.48)*	126.3 *(126.83)*	140.8 *(141.36)*	172.5 *(173.08)*
Nd	156.0 (*159.41*)	148.1 (*151.42*)	138.1 (*141.21*)	171.8 (*174.98*)
Eu	138.0 *(138.41)*	84.9 *(85.18)*	150.8 *(151.50)*	166.9 *(167.49)*
Dy	[a]	[a]	[a]	[a]
Er	100.8 (*104.92*)	69.0 (*72.40*)	138.1 (*141.69*)	143.2 (*146.88*)
Lu	148.0 (*151.07*)	125.6 (*128.65*)	140.5 (*143.58*)	171.9 (*174.96*)

[a]: only ^{1}H NMR (D_2O, 200.13 MHz, RT) spectrum have been measured δ (ppm): 42.9 (*43.1*), 38.0 (*38.1*).

In our measurements no internal standart was used, explaining the small calibration differences.

Table S3. Overview of the Ln-O and Ln N distances from [*Ln*(dipic)$_3$]3- structures availables in the Cambridge Crystallographic Data Centre.

reference	*Ln*	Ionic radius (Å)[c]	Counter ion	Average Ln-O (Å)	Average Ln-N (Å)
YUMDIT [1]	*La*	1.216	[Cr]	2.536	2.644
JUCXIO [2]	*La*	1.216	-	2.557	2.632
YUMFIV [1]	*Ce*	1.196	[Cr]	2.513	2.615
OBELUC [3]	*Nd*	1.163	NR_4	2.484	2.563
SPYCND [4]	*Nd*	1.163	Na	2.485	2.581
YOZRUA [5]	*Eu*	1.12	Cs	2.445	2.533
YOZSAH [5]	*Eu*	1.12	[Cr]	2.446	2.537
ZAYFAG [6]	*Eu*	1.12	NR_4	2.439	2.547
JEXWOY [7]	*Tb*	1.095	Na	2.421	2.506
HULDEX [8]	*Tb*	1,095	NH_4	2,422	2,500
[a]	*Dy*	1.083	Cs	2.410	2.485
NUJBAV [9]	*Ho*	1.072	NH_4	2.396	2.468
[b]	*Y*	1.075	Na	2.393	2.480
SPYCYB [10]	*Yb*	1.042	Na	2.378	2.466
NPYCYB [11]	*Yb*	1.042	Na	2.351	2.512
PYCYBN [12]	*Yb*	1.042	Na	2.335	2.380
ASUHIF [13]	*Yb*	1.042	Py+	2.369	2.453
[b]	*Lu*	1.032	Na	2.357	2.428
YUMGIW [1]	*Lu*	1.032	[Cr]	2.361	2.438

[a] O. Maury, unpublished results; [b] this study; [c] from Shannon tables see reference 10

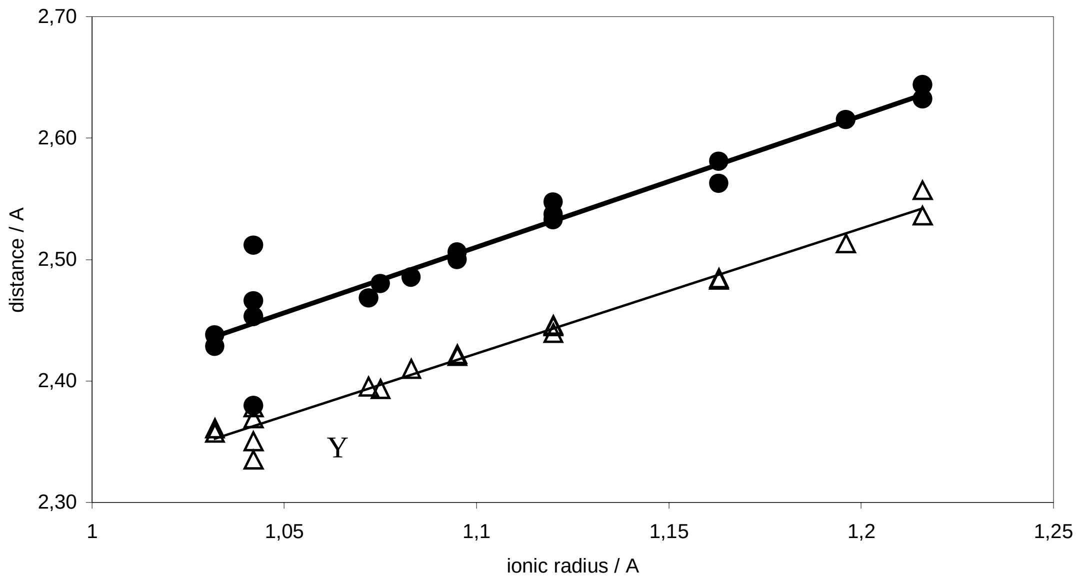

Figure S1. Plot of the Ln-N (circle) and Ln-O (triangle) distances vs lanthanide ionic radius.

Crystal data for $Na_3[\mathit{Lu}(dipic)_3].12H_2O$: Mr = 955.44, monoclinic, P 2_1/c, a = 9.6642(1) Å, b = 18.09689(2) Å, c = 17.8475(2) Å, β = 95.317(1)°, V = 3270.93(6) Å^3, Z = 4, D_X = 1.940 Mg.m^{-3}, λ(MoKα) = 0.71073Å, μ = 31.61 cm^{-1}, F(000) = 1904, T = 120 K.; 470 variables and 13782 observations with I>2.0σ(I) ; calc $w=1/[\sigma^2(Fo^2) + (0.05P)^2+21P]$ where $P=(Fo^2+2Fc^2)/3$ with the resulting R = 0.051, R_W = 0.120 and S_W= 1.024 , Δρ < 5.2 eÅ^{-3} CCDC 268181.

Crystal data for $Na_3[Y(dipic)_3]$.12H2O: Mr = 869.38, monoclinic, P2_1/c, a = 9.6914(4) Å, b = 19.1705(8) Å, c = 18.0663(7) Å, β = 97.671(3)°, V = 3355.1(2) Å^3, Z = 4, D_X = 1.721 Mg.m^{-3}, λ(MoKα) = 0.71073Å, μ = 18.78 cm^{-1}, F(000) = 1776, T = 293 K. 466 variables and 4359 observations with I>2.0σ(I) ; calc $w=1/[\sigma^2(Fo^2) + (0.069P)^2]$ where $P=(Fo^2+2Fc^2)/3$ with the resulting R = 0.060, R_W = 0.131 and S_W= 1.024 , Δρ < 0.88 eÅ^{-3} . CCDC 268182

Refernces:

1) Harrowfield, J.M.; Kim, Y.; Skelton,. B.W .; White, A.H *Aust.J.Chem*. **1995**, *48*, 807

2) Tianzhu, G.; Junkang, L.; Huizhen, Z.; Chunhui, H.; Guangxian, X.; Yuzhen, H. ; Nicheng, S. *Zhongguo Xitu Xuebao*(Chin.)(J.Chin.Rare Earth Soc.) **1991**, *9*, 97

3) Rzaczynska, Z.; Brzyska, W.; Mrozek, R.; Ozga, W.; Glowiak T. *J.Coord.Chem*. **1998**, *43* 321.

4) Albertsson, J. *Acta Chem.Scand*. **1972**, *26*, 1023.

5) Brayshaw, P.A.; Bunzli, J.-C.G.; Froidevaux, P.; Harrowfield, J.M.; Kim, Y.; Sobolev A.N. *Inorg.Chem.* **1995,** *34*, 2068.

6) Brayshaw, P.A.; Harrowfield, J.M.; Sobolev A.N., *Acta Crystallogr. ,Sect.C: Cryst. Struct. Commun*. **1995**, *51*, 1799.

7) Shengzhi, H.; Zhenchao, D.; Huizhen, Z.; Qiwang, L. Xiamen Dax. *Xuebao, Zir.Kex. (Chin.) (J.Xiamen Univ.(Nat.Sci.))* **1989**, *28*, 279.

8) Chen, L.; Yin, X.-H.; Tan, M.-Y.; Xia, C.-G.; Yu K.-B. *Acta Crystallogr. ,Sect. E: Struct. Rep. Online* **2002**, *58*, 666.

9) Brzyska, W.; Rzaczynska, Z.; Ozga, W.; Mrozek, R.; Glowiak, T. *Pol. J. Chem*. **1996**, *70*, 1008.

10) Albertsson, J. *Acta Chem.Scand*. **1972**, *26* , 1005.

11) Albertsson J. *Acta Chem.Scand*. **1972**, *26*, 985.

13) Albertsson J. *Acta Chem.Scand.* **1970**, *24*, 1213.

13) Rafizadeh, M.; Ranjbar, M.; Amani V. *Acta Crystallogr.,Sect.E:Struct.Rep.Online* **2004**, *60*, 479.